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INTERNATIONAL SYMPOSIUM ON HALIDE GLASSES (2ND)  
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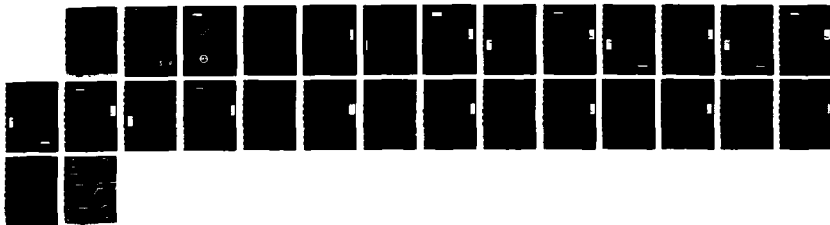
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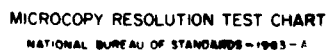
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| 1a. REPORT SECURITY CLASSIFICATION<br><b>UNCLASSIFIED</b>                                                                                                                                                                                                                                                                                                                                                              |       |                                                | 1b. RESTRICTIVE MARKINGS                                                                       |                                                     |                                |
| 2a. SECURITY CLASSIFICATION AUTHORITY<br><br><b>AD-A181 215</b>                                                                                                                                                                                                                                                                                                                                                        |       |                                                | 3. DISTRIBUTION/AVAILABILITY OF REPORT<br>Approved for public release; distribution unlimited. |                                                     |                                |
| 6a. NAME OF PERFORMING ORGANIZATION<br>Rensselaer Polytechnic Instit.                                                                                                                                                                                                                                                                                                                                                  |       |                                                | 7a. NAME OF MONITORING ORGANIZATION<br>Office of Naval Research.                               |                                                     |                                |
| 6b. OFFICE SYMBOL<br>(If applicable)                                                                                                                                                                                                                                                                                                                                                                                   |       |                                                | 7b. ADDRESS (City, State, and ZIP Code)<br>800 North Quincy Street<br>Arlington, VA 22217      |                                                     |                                |
| 6c. ADDRESS (City, State, and ZIP Code)<br>Materials Engineering Department<br>Troy, NY 12181                                                                                                                                                                                                                                                                                                                          |       |                                                | 8a. NAME OF FUNDING/SPONSORING ORGANIZATION<br>AFOSR                                           |                                                     |                                |
| 8b. OFFICE SYMBOL<br>(If applicable)<br>NC                                                                                                                                                                                                                                                                                                                                                                             |       |                                                | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER<br>AFOSR-MIPR-83-0058                          |                                                     |                                |
| 8c. ADDRESS (City, State, and ZIP Code)<br>Building 410<br>Bolling AFB, DC 20332-6448                                                                                                                                                                                                                                                                                                                                  |       |                                                | 10. SOURCE OF FUNDING NUMBERS                                                                  |                                                     |                                |
|                                                                                                                                                                                                                                                                                                                                                                                                                        |       |                                                | PROGRAM ELEMENT NO.<br>61102F                                                                  | PROJECT NO.<br>2303                                 | TASK NO.<br>A3                 |
| 11. TITLE (Include Security Classification)<br>Second International Symposium on Halide Glasses (Extended Abstracts) (U)                                                                                                                                                                                                                                                                                               |       |                                                |                                                                                                |                                                     |                                |
| 12. PERSONAL AUTHOR(S)<br>Cornelius T. Moynihan, Chairman                                                                                                                                                                                                                                                                                                                                                              |       |                                                |                                                                                                |                                                     |                                |
| 13a. TYPE OF REPORT<br>FINAL                                                                                                                                                                                                                                                                                                                                                                                           |       | 13b. TIME COVERED<br>FROM 83/06/01 TO 83/12/31 |                                                                                                | 14. DATE OF REPORT (Year, Month, Day)<br>1983/08/05 |                                |
| 15. PAGE COUNT<br>26                                                                                                                                                                                                                                                                                                                                                                                                   |       |                                                |                                                                                                |                                                     |                                |
| 16. SUPPLEMENTARY NOTATION<br>Published by Rensselaer Polytechnic Institute, August 1983                                                                                                                                                                                                                                                                                                                               |       |                                                |                                                                                                |                                                     |                                |
| 17. COSATI CODES                                                                                                                                                                                                                                                                                                                                                                                                       |       |                                                | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)              |                                                     |                                |
| FIELD                                                                                                                                                                                                                                                                                                                                                                                                                  | GROUP | SUB-GROUP                                      | halide glass                                                                                   |                                                     |                                |
|                                                                                                                                                                                                                                                                                                                                                                                                                        |       |                                                | fluoride glass                                                                                 |                                                     |                                |
|                                                                                                                                                                                                                                                                                                                                                                                                                        |       |                                                | iodide glass                                                                                   |                                                     |                                |
| 19. ABSTRACT (Continue on reverse if necessary and identify by block number)<br>This document is the Extended Abstracts of the 2nd International Symposium on Halide Glasses held at Rensselaer Polytechnic Institute, August 2-5, 1983. It contains extended abstracts of 60 papers on optical, thermal, electrical and mechanical properties of halide glasses and on their potential applications. <i>Symposium</i> |       |                                                |                                                                                                |                                                     |                                |
| 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT<br><input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS                                                                                                                                                                                                                                      |       |                                                | 21. ABSTRACT SECURITY CLASSIFICATION<br>UNCLASSIFIED                                           |                                                     |                                |
| 22a. NAME OF RESPONSIBLE INDIVIDUAL<br>Dr Donald R. Ulrich                                                                                                                                                                                                                                                                                                                                                             |       |                                                | 22b. TELEPHONE (Include Area Code)<br>(202) 767-4963                                           |                                                     | 22c. OFFICE SYMBOL<br>AFOSR/NC |

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# **Second International Symposium on Halide Glasses**

**2-5 August 1983**



**Rensselaer Polytechnic Institute  
Troy, New York 12181, USA**

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# **Second International Symposium on Halide Glasses**

In Cooperation with the Glass Division of the  
American Ceramic Society

2-5 August 1983

Rensselaer Polytechnic Institute  
Troy, New York 12181, USA

## **Industrial and Government Sponsors**

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## Objective and Background

The present Symposium is the successor to the 1st International Symposium on Halide and Other Non-Oxide Glasses which was held in March, 1982, at Cambridge University, UK. Like the first, the 2nd Symposium is intended to provide an international forum for the discussion of recent research and development in the area of halide glasses. Its purpose is to bring together those actively engaged in the field to exchange information on the physics, chemistry and applications of these materials.

It is hoped that the atmosphere of the 1st Symposium will be maintained at the 2nd Symposium. The meeting will be held in a university setting at Rensselaer Polytechnic Institute in upstate New York. Specifically, the conferees will meet, have their lodgings and take their meals all on the same site, which will maximize opportunities for interaction and information exchange among the participants.

## Symposium Extended Abstracts

Authors of invited or contributed papers have been asked to submit extended abstracts of their talks, plus copies of the important figures, tables and graphs to be used in the lecture. The extended abstracts will be reproduced, collected in a loose leaf binder and distributed to the participants at the start of the Symposium. In cases where there are last minute changes in the content of the talk, modified versions of the extended abstracts or figures may be handed in at the Symposium. These will be reproduced during the Symposium and distributed to the participants in a form that can be included in the Symposium Extended Abstracts.

## Poster Session

Poster papers reporting recent results have been encouraged from all participants and will be scheduled in the poster session. For very recent results the authors may simply arrive at the Symposium with posters in hand, and their papers will be scheduled. Authors of poster papers have been asked to bring to the Symposium copies suitable for reproduction of the important figures in their papers, as well as a title page and short abstract. These will be reproduced during the Symposium and distributed to the participants for inclusion in the Symposium Extended Abstracts.

## Lodging, Meals and Symposium Events

Participants will be housed in student residences on the RPI campus. The Symposium fee (\$165 for participants, \$130 for non-participants) includes the cost of all meals from supper on August 1 through lunch on August 5 and of all Symposium social events. The social events, which are intended to provide the participants with ample time for person-to-person discussions of halide glass science and engineering, include a reception with buffet supper on Monday evening and a clamsteak/barbecue on the RPI campus Tuesday evening. Wednesday evening will feature a scenic cruise on Lake George with a wine tasting of select New York State vintages followed by dinner on board the boat. Thursday evening the Symposium banquet will be held at the Student Prince Restaurant in the Helderberg mountains.

The main lounge of Davison Hall is available to the participants for late night discussion sessions.



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## **Symposium Schedule**

### **Monday, August 1**

12.00-23.00 Registration and reception. Commons. An informal buffet supper will be available in the reception area during the early evening.

### **Tuesday, August 2**

07.30-09.00 Continental breakfast. Davison and Sharp Halls

08.00 Registration. Communications Center, 300 level

09.00-12.25 Scientific program - Session I. All lecture sessions (I through XII) will be in the Communications Center, 300 level.

12.30-14.00 Lunch

14.00-16.35 Scientific program - Session II

17.00-18.30 Scientific Program - Poster Session. Communications Center, 200 level.

19.00-23.00 Clamsteam/barbecue. Commons lawn.

### **Wednesday, August 3**

07.30-09.00 Continental breakfast. Davison and Sharp Halls.

09.00-12.35 Scientific program - Sessions III and IV

12.35-14.00 Lunch. Commons.

14.00-17.10 Scientific program - Sessions V and VI

18.00-24.00 Dinner cruise on Lake George. Buses depart at 18.00.

**Thursday, August 4**

07.30-09.00 Continental breakfast. Davison and Sharp Halls.

09.00-12.20 Scientific program - Session VII

12.30-14.00 Lunch. Commons.

14.00-17.10 Scientific program - Sessions VIII and IX

18.00-23.00 Symposium banquet at the "Student Prince", Westerlo, NY. Buses depart at 18.00.

**Friday, August 5**

07.30-09.00 Continental breakfast. Davison and Sharp Halls.

09.00-12.35 Scientific program - Sessions X and XI

12.35-14.00 Lunch. Commons.

14.00-16.15 Scientific program - Session XII

16.15 Conclusion of Symposium

## Scientific Program and Short Abstracts

**Tuesday, August 2**

09.00      **Introductory Remarks - C.T. Moynihan**  
             **Welcome - George Ansell, Dean, School of Engineering, RPI**

### **Session I: Synthesis Techniques and Raw Materials**

*Session Chairman - C.T. Moynihan, RPI, Troy, N.Y.*

09.15      **"Early History of Heavy Metal Fluoride Glasses" - Invited Lecture**

*Michel Poulain, U. Rennes, Rennes, France*

Around 1970 a series of syntheses centered around fluorozirconates was initiated in order to find new structural types with formal  $MF_{3+x}$ . This led in 1974, to the discovery of the first  $ZrF_4$ -based glasses in the  $ZrF_4$ - $BaF_2$ - $NaF$ - $NdF_3$  quaternary system, resulting in a first paper describing the vitreous area in the  $ZrF_4$ - $BaF_2$ - $NaF$  ternary system.

Since that time, systematic work has been carried out and the synthesis methods improved. The research for new vitreous compositions was pursued, following non-classical guidelines. A predominant part was devoted to the chemical analogies suggested by the observations.

The mile-stones so far are, in 1976, barium-free fluorozirconate glasses, in 1978, a new family of fluorophosphate glasses, in 1979, the discovery of stable zirconium-free fluoride glasses in the  $ThF_4$ - $YF_3$ - $BaF_2$ - $AlF_3$  system, in 1980, that of glasses based on  $ScF_3$ ,  $ThF_4$ ,  $InF_3$  or  $LiF$  as glass progenitors, and, in the same year, the first cadmium halide glasses.

09.50      **"Synthesis of High Purity Starting Materials for Heavy Metal Fluoride Glasses" - Invited Lecture**

*M. "Sunny Jim" Robinson, Hughes Research Labs., Malibu, CA*

Methods of purifying typical fluoride glass components such as  $ZrF_4$ ,  $LaF_3$ , and  $ThF_4$  with respect to both anion and cation impurities will be described. The discussion will include purification of  $HfF_4$  and  $ZrF_4$  by sublimation in a hydrogen fluoride atmosphere and purification of individual components and glasses by reactive atmosphere processing (RAP) to eliminate the IR active impurities of  $OH^-$  and  $O^{2-}$ .

10.25      **Coffee break**

*Session Chairman - M.G. Drexhage, RADC, Hanscom AFB, MA*

10.50      **"ThF<sub>4</sub> Based Glasses: Improvement of Viscosity and Chemical Purity by Reactive Atmosphere Processing and the Addition of Doping Fluorides"**

*J. Lucas, D. Tregoeat and G. Fonteneau, U. Rennes, Rennes, France*

Reactive atmosphere processing developed by Mort Robinson at Hughes Research Labs. for the purification of fluorozirconate glasses has been extended to thorium based glasses. Specific atmospheres have been used to eliminate the parasitic -OH vibration in the 2.9  $\mu\text{m}$  region and to control the absorption caused by the M-O bond in the 8  $\mu\text{m}$  region.

The nature of the treatment, including temperature, time and the composition of the atmosphere will be discussed in relation to the oxygen content and the effects on the I.R. edge.

The influence of additive fluorides on the basic composition has been studied and related to the viscosity of the melt and the rate of devitrification. The thermal parameters and, more precisely, the variation of  $T_c$ - $T_g$ , have been followed for different compositions. The appearance of a hydroxyl band in -OH-free glasses after heating in different conditions will also be discussed.

11.10      **"Trace Impurity Analysis of Fluoride Glasses and Materials"**

*C.F. Fisher and D.C. Tran, Naval Research Lab., Washington, D.C.*

A number of selected instrumental techniques applicable for the qualitative and quantitative analysis of transition and rare earth element impurities in the ppb to ppm concentration levels in fluoride raw materials and fluorozirconate glasses are discussed. Chemical problems specific to fluoride glass analysis, such as those associated with reagent impurities, material dissolution, matrix-impurity separation and impurity reconcentration are outlined. In particular, the paper will focus on results for analysis by D.C. plasma spectrophotometry of selected transition and rare earth elements in fluoride glasses, in raw materials from various commercial sources and in laboratory prepared materials purified by sublimation and solution recrystallization.

11.30      **"Large Scale Preparation of Heavy Metal Fluoride Glasses" - Invited Lecture**

*G. Maze, Le Verre Fluore', Saint Erblon, France*

The need for fluoride glass optical components (I.R. windows, large optical items, laser rods, preforms for optical fibres, etc.) will require in the next few years large amounts of very high optical quality fluoride glasses. The best known technique for manufacturing these glasses consists in fluorinating by  $\text{NH}_4\text{HF}_2$  the mixture of oxides and fluorides. Some problems are linked to this method, e.g., phase homogeneity, dissolved gases and -OH content. This paper will discuss these problems in the light of large scale production of fluoride glasses. The possible advantages of using only fluorides as starting materials will be discussed.

A continuous manufacturing process will be presented. The general characteristics - maximum homogeneous size, -OH content, optical properties - of bulk materials manufactured by these techniques will be reviewed.

12.30            Lunch

## **Session II: Relaxation and Crystallization**

*Session Chairman - C.A. Angell, Purdue University, West Lafayette, IN*

### **14.00            "Viscosity of Some Glass-Forming Bromide Melts"**

*D. Wynne, J. Lau and J.D. Mackenzie, U. California, Los Angeles, CA*

It has been found that glass formation can take place in pure  $\text{ZnBr}_2$ , binary  $\text{ZnBr}_2$  systems such as  $\text{KBr-ZnBr}_2$ , and ternary  $\text{ZnBr}_2$  systems such as  $\text{KBr-TlBr-ZnBr}_2$ . Because viscous flow is governed by melt structure and has a direct bearing on glass formation tendency, the viscosities of a number of these bromides have been measured with a concentric cylinder method. Viscosities of these melts are compared with those of other known glass forming liquids, and the probable structures of bromide glasses are discussed.

### **14.20            "Sub- $T_g$ Aging of Heavy Metal Fluoride Glasses"**

*D.L. Gavin, A.J. Bruce, S. Loehr, S. Opalka and C.T. Moynihan, RPI, Troy, N.Y.  
M.G. Drexhage and O.H. El-Bayoumi, RADC, Hanscom AFB, MA*

Physical aging, i.e., structural relaxation or annealing, at temperatures well below the glass transition is a potential problem with heavy metal fluoride and other halide glasses because of their comparatively low  $T_g$ 's. Such physical aging might, for instance, lead to a continual drift of refractive index at ambient temperature over a period of years. An extensive investigation of physical aging in heavy metal fluoride glasses is currently underway. The glasses are annealed for periods up to several months at temperatures well below  $T_g$ , after which changes in enthalpy are measured using DSC. Preliminary results on a  $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3$  glass show rapid physical aging over a few days time  $60^\circ\text{C}$  below  $T_g$ , but thereafter the aging rate slows down markedly, in line with the expected non-linear or self-retarding character of structural relaxation. Extrapolation of the results of these experiments to predict aging rates at the use temperatures envisioned for heavy metal fluoride glasses will be discussed.

### **14.40            "Crystallization of $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3$ Glass"**

*G. Neilson, G. Smith and M. Weinberg, Jet Propulsion Labs., Pasadena, CA*

In a previous study the isothermal crystallization of  $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3$  (ZBLA) glass was

studied at 370°C. Herein, we report the results of a more extensive study of crystal formation in this glass. In particular, the crystallization tendency of ZBLA as a function of temperature and preparation procedure is discussed. X-ray diffraction and strip heater measurements have been used to detect crystallinity.

15.00        **"DSC Study of Nucleation and Crystallization of Heavy Metal Fluoride Glasses"**

*A.J. Bruce and C.T. Moynihan, RPI, Troy, N.Y.  
O.H. El-Bayoumi and M.G. Drexhage, RADC, Hanscom AFB, MA*

DSC has been used to study the effects of prior thermal treatments in the vicinity of the glass transition temperature on the crystallization behavior of a  $\text{MnF}_2$ -based, heavy metal fluoride glass. These effects will be interpreted in terms of the nucleation kinetics of the glass.

15.20        Coffee break

15.35        **"DSC Measurements of Crystal Growth Kinetics in Heavy Metal Fluoride Glasses"**

*N.P. Bansal, A.J. Bruce, R.H. Doremus and C.T. Moynihan, RPI, Troy, N.Y.*

Isothermal and non-isothermal DSC techniques have been used to study the crystal growth kinetics for a range of  $\text{ZrF}_4$ -based heavy metal fluoride glasses. Activation energies for crystal growth and Avrami exponents will be reported. The influence of glass composition on these parameters will be discussed.

15.55        **"Characterization of Crystals in Fluorozirconate Glasses"**

*G. Lu, C.F. Fisher, M.J. Burk and D.C. Tran, Naval Research Lab., Washington, D.C.*

A systematic investigation of crystallization in  $\text{ZrF}_4$ -based glasses has been undertaken. Over a dozen different morphologies have been observed in the bulk glass and characterized using optical microscopy. The most common crystals have been analyzed structurally and compositionally using micro x-ray diffraction and SEM elemental x-ray analyses. The formation of these crystals can be suppressed in certain glass compositions with proper melting conditions. The extent of drawing induced crystallization in fluoride glass fibers has also been investigated. Mie scattering theory has been employed to assess the potential effect of crystal size and refractive index on the optical attenuation in fluoro-zirconate glasses.

16.15      **"Surface Crystallization on a Fluoride Glass"**

*N.P. Bansal and R.H. Doremus, RPI, Troy, N.Y.*

The process of surface crystallization on a 62 ZrF<sub>4</sub>-33 BaF<sub>2</sub>-5 LaF<sub>3</sub> (mol %) glass composition has been studied by optical and scanning electron microscopy. The surface crystals are peculiarly wrinkled and grow out from other crystalline centers. The rate of growth of the wrinkled crystals is maximum at about 358°C and is compared with the rate of growth of bulk crystals.

17.00      **Poster Session**

**Wednesday, August 3**

**Session III: Heavy Metal Fluoride Glass Optical Fibers**

*Session Chairman - S.R. Nagel, Bell Labs., Murray Hill, N.J.*

09.00      **"Progress in Fluoride Glass Fiber Research and Development in Japan"**  
- Invited Lecture

*T. Miyashita and T. Manabe, Nippon Telephone and Telegraph, Tokai, Ibaraki, Japan*

Fluoride glass can be considered as a promising candidate material for ultra-low loss optical fibers. The Zr-Ba-Gd-Al fluoride and Zr-Ba-La-Al-Na fluoride glass systems are being investigated in Japan. A sublimation purification technique has been developed for the fluoride materials ZrF<sub>4</sub>, BaF<sub>2</sub>, GdF<sub>3</sub> and AlF<sub>3</sub>. The lowest loss of 12 dB/km at 2.55 μm has been attained in a fiber prepared by using purified materials. A fluoride glass single-mode fiber, which would be useful to take advantage of the ultra-low loss characteristic, has been prepared. The fabrication process consists of making a preform by built-in casting method, jacketing it with a tube made of the same glass as cladding, and drawing into fiber. The fiber obtained was 172 μm in total diameter, 12 μm in core diameter and had a 0.2% refractive index difference between core and clad. The current state of the art of fluoride glass fiber including the above mentioned topics will be reviewed.

09.35      **"Preparation of Heavy Metal Fluoride Glass Optical Fibers" - Invited Lecture**

*D.C. Tran and G.H. Sigel, Jr., Naval Research Lab., Washington, D.C.*

Significant technical progress in the area of ultra-low loss fiber waveguide development will be reported. This includes (1) the development of highly stable fluoride glass compositions, (2) the use of reactive atmosphere and glove box processing to eliminate OH from core and

cladding glasses, (3) the implementation of rotational casting for the fabrication of multimode and single mode fluoride glass preforms and fibers, (4) the first demonstration of ultra-low scattering losses in glass rods and drawn fibers, and (5) the optimization of the glasses to permit kilometer fiber lengths with excellent optical and mechanical properties.

10.10            **"Fluoride Glass Optical Fibers"**

*G. Maze, V. Cardin and Marcel Poulain, Le Verre Fluore', Saint Erblon, France*

Fluoride glass compositions have been investigated for the manufacturing of step index preforms. The first experiments were carried out on the most stable and best known zirconium fluoride glasses. Various size preforms were made by casting the core glass melt into a cladding tube near  $T_g$ . The geometrical and optical characteristics of the preforms were determined.

The drawing of fibers was achieved using classical devices (holder, furnace, coating equipment, drum) protected from atmospheric pollution. The resulting fibres were characterized over 15 to 100 m using a spectral loss measurement system including fluoride glass lenses for focusing. Typical transmission curves will be shown and discussed. The estimated OH concentration was around 0.2 ppm.

10.30            **Coffee break**

## **Session IV: Light Scattering, Loss Mechanisms and Coatings**

*Session Chairman - R. Jaeger, Spectran Corp., Sturbridge, MA*

11.00            **"Light Scattering in Fluoride Glasses" - Invited Lecture**

*J. Schroeder, RPI, Troy, N.Y.*

The principles of quasi-elastic and inelastic light scattering in glasses will be presented and discussed in great detail. The application of Rayleigh and Brillouin light scattering to various heavy metal fluoride glasses has resulted in valuable information on understanding the possible scattering mechanisms in these glasses. In addition, Brillouin scattering measurements allowed the calculation of the elastic and elastooptic (Pockels') coefficient of the same fluoride glasses.

The full implications that the scattering behavior has on the possible fiber optic waveguide applications of heavy metal fluoride glasses will be discussed. The physical significance of the elastic constants and elastooptic coefficients will also be considered on the basis of existing theoretical models.

11.35      **"Scattering Loss Contributions in Fluoride Glasses"**

*K.H. Levin, D.C. Tran and G.H. Sigel, Jr., Naval Research Lab, Washington, D.C.*

The sources of scattering loss were investigated in a variety of fluoride glass fibers prepared from the  $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-LiF}$  and  $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-LiF-PbF}_2$  glass systems. The low scattering fibers displayed speckle and other modal effects, which were used to determine the relative contribution of bulk and surface scattering to the total scattering loss. The differential mode scattering loss was measured, as well as the spectral loss for different launch numerical apertures. These results indicate a substantial surface scattering contribution for the low loss fluoropolymer clad fibers. The scattering centers in both high and low loss fibers were examined with an optical polarizing microscope. High loss fibers showed discrete microcrystallites and other scattering centers having diameters greater than ten microns, which were not present in low loss fibers. The results have indicated that scattering losses in fluoride glass fibers can be reduced to intrinsic levels with the use of proper glass processing and fiber drawing conditions.

11.55      **"Three Loss Mechanisms in Halide Glass Fibers"**

*H.B. Rosenstock, Naval Research Lab., Washington, D.C. and  
Sachs Freeman Associates, Bowie, MD*

As scattering and absorption of halide glasses are reduced, other optical effects limiting communication distance in fibers should be considered. The index of refraction  $n$  and hence the propagation velocity varies with frequency; this causes pulse spread for at least three different reasons: (a) frequency spread present in the original light source, (b) chopping the "monochromatic" light source into pulses, and (c) frequency shifts due to the Raman effect. We have studied effect (b) for different pulse shapes, obtaining explicit results for square as well as Gaussian pulses. The main result is a quadratic dependence of attainable propagation distance on the initial pulse width; for the few halide glasses for which  $n(\nu)$  data exist an initial pulsewidth of 1 nanosecond leads to substantial spread within several thousand km. The effect of operating around different frequencies is analyzed. The stimulated Raman effect (c) can be discussed in terms of a length  $L_a$  for amplification vs. a length  $L_s$  for separation of frequencies. The effect cannot occur if the latter is smaller.  $L_s$  again depends on the pulse width, though linearly. Thus, contrary to the trend in effect (b), this effect can be eliminated by reducing the pulse width.

12:15      **"Diamond-Like Carbon Coatings for Protection of Halide Glass Surfaces"**

*M. Stein, Stein Assoc., Bedford, MA  
A. Green, Naval Weapons Center, China Lake, CA  
B. Bendow, BDM Corp., Albuquerque, NM  
O.H. El-Bayoumi and M.G. Drexhage, RADCO, Hanscom AFB, MA*

A technique has been developed for ion-beam deposition of diamond-like carbon coatings

on halide glass surfaces. In particular, a high-adhesion carbon coating approximately 100 Å thick was deposited on a Zr-Ba-La-Al fluoride glass substrate. The initial stage consists of implantation of carbon ions at high energy, followed by a gradual reduction of ion energy over the course of the deposition. Depth profiling of the coated sample using ESCA and AES showed that the C film was reasonably pure, and the results are consistent with carbon being implanted into the substrate. A gradually decreasing trace of oxygen was observed in towards the substrate, at which point an increase in oxygen, possibly indicative of prior surface attack, was observed. The results indicate the feasibility of deposition of diamond-like carbon coatings for protection of halide glass surfaces.

12.35            Lunch

## **Session V: Transition Metal Fluoride Glasses**

*Session Chairman - D. Polk, ONR, Arlington, VA*

14.00            **"Preparation and Properties of Transition Metal Fluoride Glasses"**  
- Invited Lecture

*C. Jacobini, U. Maine, LeMans, France*

A large family of new fluoride glasses has been investigated in the  $\text{PbF}_2\text{-M}_1^{\text{II}}\text{F}_2\text{-M}_2^{\text{III}}\text{F}_3$  systems ( $\text{M}_1 = 3d$  transition metal, Ga or In). The most stable glasses belong to  $\text{PbF}_2\text{-MnF}_2\text{-M}_2^{\text{III}}\text{F}_3$  system ( $\text{M}_2^{\text{III}} = \text{Fe}^{3+}, \text{Ga}^{3+}$ ). For standard lead fluoride glasses, the glass transition lies around 280°C and fusion at 550°C; the density is about 5.5 g/cm<sup>3</sup> and the refractive index in the range 1.58-1.63. For both  $\text{PbF}_2\text{-MnF}_2\text{-FeF}_3$  and  $\text{PbF}_2\text{-MnF}_2\text{-GaF}_3$  glasses the I.R. transparency is excellent up to 8 μm (for 3mm thickness). Typical spin-glass behavior has been found for fluoride glasses in the  $\text{PbF}_2\text{-MnF}_2\text{-FeF}_3$  system ( $5\text{K} < \theta_p < 12\text{K}$ ). Neutron diffraction measurements in the paramagnetic state and in the frozen state have given structural information about the paramagnetic species. Recent EXAFS studies on the Mn, Fe and Pb absorption edges have confirmed the sixfold coordination of the paramagnetic ions and a ninefold coordination for  $\text{Pb}^{2+}$  ions. It now seems possible to propose a short distance model (8 - 9 Å) which agrees with magnetic, neutron, EXAFS and RMN data.

14.35            **"ThF<sub>4</sub>/MnF<sub>3</sub> Based Glasses: Recent Developments"**

*J. Lucas, Y. LePage and G. Fonteneau, U. Rennes, Rennes, France*

In order to stabilize heavy metal fluoride glasses based on  $\text{ThF}_4$  and  $\text{MnF}_2$ , the quaternary system  $\text{ThF}_4\text{-MnF}_2\text{-BaF}_2\text{-LnF}_3$  with  $\text{Ln} = \text{Y}, \text{Yb}$  has been investigated. Absorption measurements in the U.V. region show the influence of the paramagnetic  $\text{Mn}^{2+}$  on the U.V. transmission. Magnetic susceptibility and spectroscopic studies indicate that manganese

remains in its bivalent state even after preparation in room atmosphere. Results concerning the I.R. transmission in the  $8\ \mu$  region will be presented in relation to oxygen content. The influence of some reactive atmosphere processing treatments, which eliminate the OH absorption, will also be discussed. Chemical durability has been investigated, first, in highly oxidizing conditions, for example,  $F_2$  atmosphere at  $300^\circ\text{C}$ , with evidence of  $Mn^{3+}$  formation and second, in moist atmosphere during the annealing process.

#### 14.55 "Fluoride Glasses of Uranium IV and 3d Transition Metals"

*J. Guery, G. Courbion, C. Jacobini and R. DePape, U. Maine, LeMans, France*

New fluoride glasses with composition  $BaF_2-M_iF_n-UF_4$  ( $M_iF_n = MnF_2, FeF_2, CuF_2, ZnF_2, TiF_3, VF_3, FeF_3, GaF_3$ ) have been prepared. Large samples ( $20 \times 8 \times 8\ \text{mm}^3$  for example) can be obtained for  $33BaF_2-33\ FeF_3-33\ UF_4$  glass. The vitreous regions have been established for  $M_iF_n = MnF_2, ZnF_2, FeF_3$ . For standard glasses, the glass transition lies around  $333^\circ\text{C}$  and fusion at  $620^\circ\text{C}$ . The density is about  $5.6\ \text{g/cm}^3$  and the refractive index in the range 1.50-1.55. The chemical resistance to water attack is excellent. The absorption spectrum in the visible region is consistent with the  $4^+$  oxidation state of uranium. Systematic studies of the magnetic behavior of  $U^{4+}$  in these glasses have been performed. In the paramagnetic state ( $T > 100\text{K}$ ) the Bohr magneton number ( $\mu_B$ ) is identical to that of  $U^{4+}$  in crystalline compounds. As in the 3d transition metal fluoride glasses, the antiferromagnetic interactions are preponderant ( $-100\text{K} < \theta_p < -30\text{K}$ ). The effects of dilution by diamagnetic cations such as  $Zn^{2+}$  or  $Th^{4+}$  will be discussed.

15.15 Coffee break

## Session VI: Mechanical Properties

*Session Chairman - P.K. Gupta, Case-Western Reserve U., Cleveland, OH*

#### 15.35 "Mechanical Behavior of Heavy Metal Fluoride Glasses" - Invited Lecture

*J.J. Mecholsky, Sandia Nat'l Labs., Albuquerque, NM*

Compositional changes in fluoride glasses can affect mechanical properties such as microhardness, stress corrosion susceptibility and fracture toughness. The fracture toughness of fluoride glasses range from  $0.2$  to  $0.4\ \text{MPa m}^{1/2}$  depending on composition. A systematic change in composition of heavy metal fluoride glasses containing ytterbium or yttrium demonstrates that compositions can be optimized for mechanical properties. These glasses are mechanically superior to fluorozirconates and fluorohalifates. The difference in fracture toughness between measurements in oil and water is an indirect measure of stress corrosion susceptibility. Some compositions show no difference in fracture toughness between air and water. This suggests that compositions can be fabricated with high resistance to stress corrosion.

16.10      **"Mechanical Properties of Infrared Transmitting Fibers"**

*P.W. France, S.F. Carter, J.R. Williams and K.J. Beales, British Telecom Labs., Suffolk, UK*

Strength and static fatigue of infra-red transmitting fibres have been measured using a two-point bending technique. Single material fibres of GeAsSe and  $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-LiF}$  were drawn by a crucible technique and in-line coated with UV-cured epoxy-acrylate or silicone resin. The median ambient failure strain of the GeAsSe fibre was 3.9% which is similar to many multicomponent oxide glasses. However, because the Young's modulus is only 15.5 GPa, this corresponds to median failure stress of 0.57 GPa. Measurements of dynamic fatigue and results in liquid nitrogen and water indicate that these glasses do not exhibit stress corrosion in humid environments, and this is a significant result for long-term communication systems. Strength and dynamic fatigue of fluoride glasses are currently being measured and these results will be presented at the conference.

16.30      **"Environmental Effects on the Strength of Fluoride Glass Fibers"**

*A. Nakata, J. Lau and J.D. Mackenzie, U. California, Los Angeles, CA*

Both the chemical durability and strength of bulk fluorozirconate glasses are known to be substantially lower than those of silicates. It is also known that strength is adversely affected by surface attack. This paper is concerned with the effects of various ambient atmospheres on the strength of fluoride glass fibers. The tensile strengths of fluorozirconate fibers coated with Teflon FEP have been studied as a function of time in a 100% relative humidity atmosphere at room temperature and in a 99.998% pure dried nitrogen atmosphere.

16.50      **"Effect of NaF Additions Upon the Mechanical Behavior of Fluorozirconate Glasses"**

*A. Tesar, R.C. Bradt and C.G. Pantano, Pennsylvania State U., University Park, PA*

The relationships between glass composition, structure and mechanical behavior have been examined in the system  $0.60\text{ZrF}_4\text{-}0.30\text{BaF}_2\text{-}0.08\text{LaF}_3\text{-}0.03\text{AlF}_3\text{-}x\text{NaF}$ . The elastic constants, fracture toughness and stress corrosion susceptibilities will be presented. The glasses were characterized by wet chemical analysis, differential scanning calorimetry, infrared spectroscopy, density and refractive index measurements. It appears that although small additions of NaF increase the glass forming ability, they decrease the fracture toughness.

**Thursday, August 4**

**Session VII: Mechanical Properties (cont.) and New Vitreous Fluoride Systems**

*Session Chairman - D. Uhrich, AFOSR, Washington, DC*

**09.00 "Fracture Analysis of Fluoride Glass Fibers"**

*J.J. Mecholsky, Sandia Nat'l Labs., Albuquerque, NM  
J. Lau and J.D. Mackenzie, U. California, Los Angeles, CA  
D. Tran, Naval Research Lab., Washington, D.C.  
B. Bendow, BDM Corp., Albuquerque, NM*

Fractographic analysis was performed on Teflon coated, core-clad alkali fluorozirconate glass fibers. The fracture surfaces appear similar to those observed for silicate and chalcogenide glass fibers, with a majority of the breaks originating near the outer surface of the fiber. The measured tensile strengths vary widely, with some fibers displaying values in excess of 50 kpsi.

**09.20 "Recent Progress in Halide Glass Research at the University of Rennes"  
- Invited Lecture**

*J. Lucas, U. Rennes, Rennes, France*

Three main complementary aspects of halide glass research have recently been explored at Rennes:

- a) The first, which is something of a home tradition, is the research of original compositions giving vitreous materials. The most significant result is the discovery of a new family of glasses based on cadmium halides, which display interesting transmission properties in the I.R.
- b) The second is the optimization of known fluoride glasses, in the hope of developing good technical materials. Studies of the nucleation and crystallization mechanisms have produced interesting results. The field of thorium-based glasses has been thoroughly investigated in order to obtain oxygen-free materials, to improve the viscosity without modifying the I.R. transmission, and to decrease the rate of devitrification by modifying the composition.
- c) The final aspect concerns practical investigation of structure using X-Ray and spectroscopy and conceptual studies of the conditions of halide glass formation. This allows us to give a probable model for fluorozirconate glasses which will be presented and discussed in detail.

09.55      **"Effect of Alkali Fluoride Additions on Properties of BaF<sub>2</sub>/ThF<sub>4</sub> Glasses"**

*S. Loehr, A.J. Bruce, K.-H. Chung and C.T. Moynihan, RPI, Troy, NY  
M.G. Drexhage, RADC, Hanscom AFB, MA*

For a parent BaF<sub>2</sub>-ZnF<sub>2</sub>-YbF<sub>3</sub>-ThF<sub>4</sub> glass of 19:27:27:27 mol% composition the addition of 5 mol% NaF or KF at the expense of BaF<sub>2</sub> has little effect on the absorption coefficients on the intrinsic multiphonon edge over a frequency range of 800-1400 cm<sup>-1</sup>. Addition of 5 mol% LiF increases the absorption coefficients significantly, with a two-fold increase at 1300cm<sup>-1</sup>. The addition of 5 mol% NaF or LiF increases the ease of formation of the glass as measured by the (T<sub>x</sub>-T<sub>g</sub>)/T<sub>g</sub> ratio, NaF to a greater extent than LiF. The addition of 5% KF markedly decreases the ease of glass information.

10.15      **"CALPHAD Calculation of Quaternary Fluoride Glass Composition"**

*L. Kaufman and D. Birnie, ManLabs Inc., Cambridge, MA*

The CALPHAD method for coupling thermochemical and phase diagram data on binary systems for the purpose of calculating ternary and higher order phase diagrams has been applied to establishing a data base for fluoride systems relevant to glass formation and calculating isothermal sections in the LaF<sub>3</sub>-ZrF<sub>4</sub>-BaF<sub>2</sub> and the BaF<sub>2</sub>-ZrF<sub>4</sub>-NaF systems. The latter calculations disclosed the compositions of maximum liquid phase stability, i.e., lowest liquidus temperature, which in turn were found to contain the composition ranges in which glass formation has been observed experimentally. The present work extends the calculation to the quaternary system LaF<sub>3</sub>-ZrF<sub>4</sub>-BaF<sub>2</sub>-AlF<sub>3</sub> containing up to 15 mol% AlF<sub>3</sub> in order to illustrate the level of agreement between multicomponent calculations of liquid phase stability and the observed range of glass forming compositions.

10.35      **Coffee break**

*Session Chairman - R.C. Folweiler, GTE Labs., Waltham, MA*

11.00      **"Multicomponent Heavy Metal Fluoride Glasses Containing MgF<sub>2</sub>"**

*O.H. El-Bayoumi and M.G. Drexhage, RADC, Hanscom AFB, MA  
J.R. Gannon and P. Tick, Corning Glassworks, Corning, NY*

Glass formation has been discovered in a number of systems containing MgF<sub>2</sub> and ZnF<sub>2</sub> in conjunction with PbF<sub>2</sub>, YbF<sub>3</sub>, AlF<sub>3</sub> or ThF<sub>4</sub>. While many compositions require rapid quenching, others such as (mol%) 8.5 MgF<sub>2</sub>-25.5 ZnF<sub>2</sub>-25.5 YbF<sub>3</sub>-25.5 ThF<sub>4</sub>-15 AlF<sub>3</sub> glass may be cast to yield transparent specimens ~ 3 mm thick by several cm on a side. Efforts to further stabilize such glass are described. Analysis of the crystalline phases in devitrified glasses shows them to be rich in Al and Yb. The optical, physical and thermal properties of these new glasses are discussed.

11.20      **"ThF<sub>4</sub> and LiF - Based Fluoride Glasses"**

*Michel Poulain and Marcel Poulain, U. Rennes, Rennes, France*

Numerous fluoride glasses include variable amounts of ThF<sub>4</sub>. This paper is centered upon new glasses in fluoride systems associating ThF<sub>4</sub> with alkali or alkaline earth fluorides. The limits of glass formation by quenching have been settled in the ThF<sub>4</sub>-LiF-BaF<sub>2</sub>, ThF<sub>4</sub>-LiF-NaF, ThF<sub>4</sub>-LiF-KF and ThF<sub>4</sub>-LiF-KF-NaF systems. Some related compositions will be given. The alkali concentration may be unusually high (60-90%). Binary glasses (Th<sub>0.3</sub>Li<sub>0.7</sub>)F<sub>1.9</sub> and (Th<sub>0.2</sub>Na<sub>0.8</sub>)F<sub>1.8</sub> have been prepared by rapid quenching. With the most stable compositions, which include ThF<sub>4</sub> and LiF, samples of a thickness of 3 mm may be obtained. They are stable in room atmosphere and also in aqueous solutions at 20°C. For a typical composition 0.3 ThF<sub>4</sub>-0.6 LiF-0.1 BaF<sub>2</sub> the characteristic temperatures are T<sub>g</sub>=256°C, T<sub>c</sub>=310°C and T<sub>f</sub>=560°C, the refractive index is n<sub>D</sub>=1.4945 and the density is 5.29 g/cm<sup>3</sup>. These glasses are transparent in the I.R. spectrum only up to 6 microns, as are AlF<sub>3</sub>-based glasses, because of the major contribution of lithium to the multiphonon absorption.

11.40      **"Optical Properties of Fluorophosphate Glasses"**

*B. Kumar and R. Harris, U. Dayton, OH*

Glass compositions from the AlF<sub>3</sub> - (Ca+Sr+Ba) F<sub>2</sub> - P<sub>2</sub>O<sub>5</sub> system have been synthesized under varied melting conditions. Optical properties such as U.V. absorption edge, IR transmission, temperature coefficient of refractive index and absorption coefficients at 1.30 μm have been determined. Variation in the optical properties with compositional changes and melting conditions will be discussed and presented.

12.00      **"The Structure and Properties of Pure and Nd Doped BeF<sub>2</sub> Based Glasses"**

*L.D. Pye, S.C. Cherukuri and I. Joseph, Alfred U., Alfred, NY*

The optical/magnetic properties (Faraday effect) of a series of fluoride based glasses have been studied. Additionally, we report on our attempts to computer simulate the structure of pure non-crystalline BeF<sub>2</sub> by a novel method.

12.30      **Lunch**

## **Session VIII: Lasing and Luminescence in Fluoride Glasses**

*Session Chairman - G.H. Sigel, Jr., Naval Research Lab., Washington, D.C.*

### **14.00 "Heavy Metal Fluoride Glasses as Mid-IR Laser Materials" - Invited Lecture**

*W. Sibley and M.D. Shinn, Oklahoma State U., Stillwater, OK*

A study using broad band excitation of the optical absorption, emission and excitation spectra of  $\text{Er}^{+3}$  and  $\text{Ho}^{+3}$  ions in a fluorozirconate glass has been carried out as a function of temperature. Radiative and non-radiative transition rates have been characterized via a number of models or theories. The optical properties of  $\text{Er}^{+3}$  and  $\text{Ho}^{+3}$  doped fluorozirconate glasses are similar to those of  $\text{Er}^{+3}$  doped crystals.

### **14.35 "Optical and Lasing Properties of Nd(III)-Doped $\text{BeF}_2$ Glasses"**

*M.J. Weber, C.F. Cline, G.J. Linford, D. Milam, S.E. Stokowski and  
S.M. Yarema, Lawrence Livermore Nat'l Lab., Livermore, CA*

Beryllium fluoride glasses have the largest band gaps and smallest refractive index nonlinearities reported for any glasses. These glasses are therefore of interest for optical elements and amplifying media in lasers operating at short wavelengths and high powers. Studies of spectroscopic properties of  $\text{Nd}^{3+}$  show that the stimulated emission cross sections for the  $^4\text{F}_{3/2} - ^4\text{I}_{11/2}$  transition can be varied by a factor of about three by changing the beryllium fluoride glass composition. We have measured the small-signal gain of both low cross section  $\text{BeF}_2$  glass and a high cross section K-Ca-Al fluoroberyllate glass. The resulting gain coefficients are in reasonable agreement with predictions made using spectroscopic data and a flashlamp pumping model. We have also investigated lasing in the large-signal gain regime. The effective saturation parameter increased with increasing output fluence, thereby demonstrating the presence of hole burning arising from spectroscopic inhomogeneities. The optical and lasing properties of beryllium fluoride glasses are compared with those obtainable from oxide and oxyfluoride glasses.

### **14.55 "Energy Transfer Between Mn(II) and Er(III) in a Gallium Lead Fluoride Glass"**

*R. Reisfeld and E. Greenberg, Hebrew U., Jerusalem, Israel  
C. Jacobini and R. DePape, U. Maine, LeMans, France  
C.K. Jørgensen, U. Geneva, Geneva, Switzerland*

The luminescence yields of both the lowest quartet state of  $3d^5 \text{Mn(II)}$  and the fourth and fifth excited J-levels  $^4\text{F}_{9/2}$  and  $^4\text{S}_{3/2}$  (emitting at 550 nm) of  $4f^{11} \text{Er(III)}$  are unusually high in fluoride glasses (corresponding to only weak competition by non-radiative de-excitation). The decay

is not exponential, but the mean life-time 0.06 ms of  $^4S_{3/2}$  is decreased to 0.01 ms in presence of Mn(II), providing a broader emission at 630 nm.  $^4F_{9/2}$  emitting at 668 nm (life-time 0.08 ms shortened by Mn to 0.025 ms) is below the lowest Stokes threshold of any Mn(II) site, but can be efficiently fed by the long-lived quartet (1.4 ms without erbium present) with the result that 668 nm emission of a mixed sample has a short-lived, intense component (much weaker by 370 nm excitation in the absence of manganese) and a weak, long-lived emission paid back by Mn(II) storing the energy. Other results of mutual energy transfer and cascading-down are observed by excitation below 400 nm, and the probability of mutual energy transfer is theoretically evaluated.

15.15      Coffee break

## **Session IX: Fundamental Optical Phenomena**

*Session Chairman - J.R. Gannon, Corning Glassworks, Corning, NY*

15.35      **"Fundamental Optical Properties of Heavy Metal Fluoride Glasses"**  
- Invited Lecture

*B. Bendow, BDM Corp., Albuquerque, NM*

Extensive studies have been conducted recently on the fundamental optical properties of heavy metal fluoride glasses. Although the data is far from comprehensive, considerable information is nevertheless available for many glasses, covering properties such as IR and UV absorption, fundamental IR reflectivity, refractive index, dispersion and  $dn/dT$ , Raman, Brillouin and Rayleigh scattering and photoelastic constants. Moreover, significant progress has been made in determining the dependence of optical properties on glass composition. A sampling of the many conclusions which may be drawn from recent work includes the following: (a) The frequency and temperature dependence of IR edges is similar to that of crystals, although the dependence on composition differs. (b) Raman and IR spectra are sharper than those of most glasses, but broader than those of crystals. (c) The dispersion is low over a broad range of frequencies. (d) Rayleigh scattering can be lower than for oxide glasses. (e) Ultra-low values of thermal distortion can be achieved by varying composition.

16.10      **"A Vibrational Spectroscopy Study of the Structure of Binary Thorium Fluorohafnate Glasses"**

*R.M. Almeida, U. Lisbon, Lisbon, Portugal*  
*J.D. Mackenzie, U. California, Los Angeles, CA*

A series of glasses were prepared in the  $HfF_4$ - $ThF_4$  system, which did not include a modifier, and its glass-forming region was determined. Glass transition and crystallization

temperatures were measured by Differential Thermal Analysis. Infrared absorption, infrared reflection and polarized Raman spectra have been recorded for several different compositions. The results were compared with those previously obtained for binary  $\text{HfF}_4$ - $\text{BaF}_2$  and  $\text{ZrF}_4$ - $\text{ThF}_4$  glasses and crystalline  $\text{HfF}_4$  and  $\text{ThF}_4$ , and the main vibrational modes were assigned. The infrared absorption and particularly the Raman spectra of the  $\text{HfF}_4$ - $\text{ThF}_4$  glasses were significantly different from those of  $\text{HfF}_4$ - $\text{BaF}_2$  glasses. The substitution of a network modifier such as  $\text{BaF}_2$  by a network former like  $\text{ThF}_4$  substantially increases the degree of bridging and appears to change the structure from a predominantly one-dimensional type to a three-dimensional network. The most probable coordinations for Hf and Th atoms are also discussed.

#### 16.30 "Raman Scattering in $\text{ZrF}_4$ Based Glasses"

*J.A. Freitas, Jr., R.P. Devaty, D.C. Tran and U. Strom, Naval Research Lab., Washington, D.C.*

Raman spectra of glasses prepared (by J.D. Mackenzie) with the approximate composition (in mole %) 62%  $\text{ZrF}_4$ , 30%  $\text{BaF}_2$ , 8%  $\text{LaF}_3$  have been studied with a 5145 Å exciting laser line at 300K. Some of the glasses were doped with different concentrations of oxygen (either  $\text{La}_2\text{O}_3$  or  $\text{ZrO}_2$ ). One glass sample was doped with cerium ( $\text{CeF}_3$ ). In addition, all glasses contained some  $\text{OH}^-$ , as well as different concentrations of transition metal impurities other than Ce. The Raman spectra were found to be insensitive to the presence of  $\text{OH}^-$ , oxygen and Ce impurities. On the other hand, the Raman spectra were observed to be significantly dependent on the concentration of transition metal (TM) impurities (other than cerium) as measured by optical transmission and electron spin resonance (ESR) techniques. For glasses with low concentrations of TM impurities the Raman spectra are dominated by the strong, highly polarized mode near  $580\text{ cm}^{-1}$  which has been previously observed by Almeida and Mackenzie as well as Banerjee, et al. We find that the magnitude of the  $580\text{ cm}^{-1}$  mode decreases proportionally with an increasing concentration of TM metal impurities, whereas there is a concomitant increase in Raman activity near 130, 250, 1000 and  $1250\text{ cm}^{-1}$ . ESR and optical transmission measurements provide strong evidence for the presence of Fe and Mn in these glasses. We suggest that these impurities disturb the highly symmetric  $\text{ZrF}_4$  planar configurations leading to suppression of the associated highly polarized Raman modes and a simultaneous increase in the intensity of nonpolarized Raman modes.

#### 16.50 "Polarized Raman Spectra of Ca/Sr/Al Fluorophosphate Glasses"

*P. K. Banerjee and S.S. Mitra, U. Rhode Island, Kingston, RI  
B. Kumar, U. Dayton, Dayton, OH  
B. Bendow, BDM Corp., Albuquerque, NM*

An investigation of the vibrational characteristics of fluorophosphate glasses was conducted using polarized Raman scattering and fundamental IR reflectivity measurements. Two strong, highly polarized bands are observed in Raman; these are assigned to Al-F vibrations. Two relatively weak, but polarized, Raman bands are assigned to P-O vibrations. We conclude that the glass contains two types of well-defined structural units associated with  $\text{AlF}_3$  and  $\text{P}_2\text{O}_5$  and that the alkaline earth ions are distributed outside of these units.

**Friday, August 5**

**Session X: Structure and Properties**

*Session Chairman - J. Lucas, U. Rennes, Rennes, France*

**09.00 "Structure of Heavy Metal Fluoride Glasses" - Invited Lecture**

*Marcel Poulain, U. Rennes, Rennes, France*

The structural studies carried out so far upon heavy metal fluoride glasses (Raman, I.R., NMR and X-ray diffraction) indicate that there is no significant change in the chemical behavior of the vitrifying cation in glass or in crystalline material. Fluoride glass structure may be described by means of a network model which is constructed from the coordination polyhedra of the higher charged cations. An alternative model is the random packing of spheres, which accounts for the importance of the modifiers and encompasses glass formation in mixed halide systems. It applies for most ionic glasses and suggests some relationship with metal glasses. The kinetic aspects of glass formation are related to the electrostatic interactions in the ion distribution. The occurrence of non-tetrahedral glasses is opening a large field of investigations which benefits glass science and solid state chemistry.

**09.35 "An  $F^{19}$  NMR Study of Heavy Metal Fluoride Glasses Based on  $ZrF_4$ "**

*P.J. Bray and R.V. Mulkern, Brown U., Providence, RI  
M.G. Drexhage, RADC, Hanscom AFB, MA  
S. Greenbaum and D.C. Tran, Naval Research Lab., Washington D.C.*

$F^{19}$  NMR has been used to investigate fluorine ionic motion in several glass systems based on  $ZrF_4$ . Spin-lattice relaxation rates ( $T_1$ ) of  $F^{19}$  as a function of temperature have yielded activation energies for fluorine diffusion. The results indicate a significant dependence on sample composition. CW motional narrowing experiments have been used to determine the relative amounts of mobile and stationary fluoride ions as a function of temperature.

**09.55 "Neutron Diffraction and Molecular Dynamics Studies of Vitreous  $NaF-DyF_3-BeF_2$ "**

*A.C. Wright and G. Etherington, J.J. Thomson Physical Lab., Reading, UK  
S.A. Brawer and M.J. Weber, Lawrence Livermore National Lab., Livermore, CA  
R.N. Sinclair, AERE, Harwell, UK*

Rare earth containing fluoroberyllate glasses are of considerable interest in view of their possible application in the high powered lasers being developed for the laser fusion programme. At present, however, the local environment of the rare earth ions in such glasses, which determines their spectral properties, has not been established.

Neutron diffraction techniques have, therefore, been used to investigate the structure of vitreous NaF-BeF<sub>2</sub> containing DyF<sub>3</sub>. Dy is a particularly favorable element for neutron diffraction in that it can be obtained as a mixture of isotopes such that the coherent neutron scattering length is zero. Thus by studying the difference between the diffraction patterns for samples containing natural and zero scattering length Dy, it is possible to experimentally isolate the Dy-X + Dy-Dy and X-X + Dy-Dy (X = Na, Be or F) contributions to the real space correlation function and hence probe the Dy environment directly. Additional samples of undoped NaF-BeF<sub>2</sub> and pure BeF<sub>2</sub> have also been studied. The results of the neutron diffraction experiments on the three glasses (NaF-DyF<sub>3</sub>-BeF<sub>2</sub>, NaF-BeF<sub>2</sub> and BeF<sub>2</sub>) will be compared to the predictions of molecular dynamics simulations of similar compositions, particularly in respect of the Dy-F and Be-F bond length distributions.

10.15      **"Thermal Conductivity of Several Halide Glasses"**

*H.H. Sample and K.A. McCarthy, Tufts U., Medford, MA*

Measurements of the thermal conductivity of several halide glasses are being made in the 1.5 - 400K temperature range. These glasses include fluoride glasses from the Naval Research Laboratory and bismuthate glasses from Corning Glassworks. The thermal conductivity in the 1.5 to 100 K temperature region is measured via the steady state method, using a cryostat previously described. The thermal conductivity at temperatures greater than 100 K is measured using a comparative method in which Pyrex 7740 is the standard material. These results will be compared with our earlier results on a fluorozirconate glass (ZBLAN glass).

10.35      **Coffee break**

## **Session XI: Chemical Durability and Surfaces**

*Session Chairman - O.H. El-Bayoumi, RADC, Hanscom AFB, MA*

11.00      **"Chemical Durability Studies of Heavy Metal Fluoride Glasses"**  
              **- Invited Lecture**

*C.J. Simmons, Catholic U. of America, Washington, D.C.*

The chemical dissolution behavior of several classes of heavy metal fluoride glasses was studied. Results of solution analysis, infrared spectroscopy, SEM and EPMA are reported and show significant differences in leach rates between HfF<sub>4</sub>/ZrF<sub>4</sub> based glasses and those containing ThF<sub>4</sub>.

11.35      **"Dissolution of Fluorozirconate Glasses"**

*T.A. McCarthy and C.G. Pantano, Pennsylvania State U., University Park, PA*

The kinetics and pH dependence of dissolution of fluoro-zirconate glasses has been investigated. A series of ZBLA glasses with varying amounts of NaF were examined. The dissolution rates were measured in deionized water at 30°C, 60°C and 90°C, as well as in solutions of pH 2 and pH 10. Initially, there is a preferential release of fluorine and a corresponding decrease in pH. This is also observed under high pH conditions. However, once the pH stabilizes, the solution attains a composition whose cation to anion ratio is stoichiometric with the glass. Very often, the crushed glass specimens are completely transformed into a hydrated crystalline material. A dissolution mechanism is proposed based upon the pH, temperature and composition dependences of the dissolution kinetics and alteration products.

11.55      **"Nuclear Reaction Analysis and Rutherford Backscattering Spectrometry in the Study of the Reaction between Fluoride Glasses and Water"**

*W.A. Lanford and C. Burman, SUNY Albany, Albany, NY  
R.H. Doremus, RPI, Troy, NY*

The study of the reaction between water and the surfaces of halide glasses is both technologically important and of fundamental interest in the study of aqueous corrosion. Since some fluoride compounds are known to be  $F^-$  ionic conductors, an important reaction mechanism might be ionic exchange and interdiffusion involving  $F^-$  from the glass and  $OH^-$  from surface water, analogous to the  $Na^+ - H_3O^+$  ionic exchange and interdiffusion that operates in the reaction between water and alkali (soda) glasses. We have examined the reaction between a Zr, Ba, La fluoride glass and water by studying the changes in the elemental composition of the glass surface resulting from exposure to water. Quantitative concentration profiles of hydrogen are measured by nuclear reaction analysis and profiles of the other elements present are measured by Rutherford backscattering. The results show that this glass is less durable than common soda-lime glasses, since even a short exposure to water results in large changes in the near surface compositions. These experimental procedures and results will be discussed in light of the present understanding of reaction mechanisms.

12.15      **"Surface Studies of Fluorozirconate Glasses"**

*C.A. Houser and C.G. Pantano, Pennsylvania State U., University Park, PA*

Secondary ion mass spectroscopy (SIMS), sputter induced photon spectroscopy (SIPS), and scanning electron microscopy (SEM) have been used to examine the surface structure and the in-depth distribution of F, H, OH and metal-ions in fluoro-zirconate glasses. The effects of polishing in a variety of media was examined for practical reasons, as well as to

define a surface preparation method suitable for subsequent hydration studies. The effects of humidity and exposure to a variety of aqueous solutions upon the in-depth concentration profiles were then investigated. The hydration behavior in glasses with systematically varying NaF contents has also been examined. In general, the formation of hydrated surface layers is quite extensive in aqueous solutions.

12.35            Lunch

## **Session XII: Chloride, Bromide and Iodide Glasses**

*Session Chairman - P. Bray, Brown U., Providence, RI*

### **14.00            "Halide Glasses Based on Chlorides, Bromides and Iodides" - Invited Lecture**

*J.D. Mackenzie, U. California, Los Angeles, CA*

There is little information on glasses based on chlorides, bromides and iodides. This paper is a review on these halide glasses and a comparison between them and the more common fluoride glasses. The glass formation aspects, the known and expected properties and the structures of these glasses are discussed.

### **14.35            "Far-IR Transmitting Cadmium Iodide Based Glasses"**

*E.I. Cooper and C.A. Angell, Purdue U., W. Lafayette, IN*

A new classic of inorganic halide glasses is described, in which iodide is either the only or the main anion. The glass-formation progenitor is  $\text{CdI}_2$  (usually 40-60 mol%); other components used were  $\text{CsI}$ ,  $\text{KI}$ ,  $\text{TlI}$ ,  $\text{PbI}_2$ , the corresponding bromides, etc. The iodide glasses exhibit remarkably high far-IR transmittance (down to  $350 \text{ cm}^{-1}$  for 2 mm thick plates), and a much better resistance to humidity than that of known chloride glasses; however the low glass-transition temperatures ( $10\text{-}35^\circ\text{C}$ ) lead to relatively poor stability. High lead halide content "marginal" glasses of higher  $T_g (\leq 63^\circ\text{C})$  and excellent moisture resistance are briefly described.

### **14.55            "Progress in Cadmium Halide Glasses"**

*M. Matecki, Michel Poulain and Marcel Poulain, U. Rennes, Rennes, France*

The glass forming ability of cadmium halides  $\text{CdF}_2$  and  $\text{CdCl}_2$  has been demonstrated in fluoride, chloride and mixed halide systems. The vitreous areas have been determined in the fluoride, chloride and mixed halide systems. The vitreous areas have been determined in the following ternary systems:  $\text{CdF}_2\text{-BaF}_2\text{-ZnF}_2$ ,  $\text{CdCl}_2\text{-BaCl}_2\text{-KCl}$  or  $\text{NaCl}$ ,  $\text{CdCl}_2\text{-CdF}_2\text{-BaF}_2$  and  $\text{CdCl}_2\text{-CdF}_2\text{-BaCl}_2$ . Only small sheets may be obtained for the monohalide glasses hygroscopic, but the introduction of fluorine prevents damage by moisture. In a typical

composition of  $0.3 \text{ CdCl}_2\text{-}0.4 \text{ CdF}_2\text{-}0.3 \text{ BaF}_2$ ,  $T_g$  occurs at  $182^\circ\text{C}$ ,  $T_c$  at  $216^\circ\text{C}$  and  $T_m$  at  $443^\circ\text{C}$ . The I.R. multiphonon absorption edge lies between 9 and 14 microns for samples of 1 mm in thickness. Cadmium halide glasses display an intermediate character between  $\text{ZnF}_2$ - and  $\text{ZnCl}_2$ -based glasses and bismuth halide glasses. They appear to be a new class of vitreous materials with potential applications for I.R. transmission and low-loss optical fibres.

15.15            Coffee break

15.35            **"New Halide Glasses in the  $\text{CuCl-CsBr-PbBr}_2$  System"**

*T. Yamagishi, J. Nishii and Y. Kaite, Nippon Sheet Glass Co., Itami City, Japan*

The glass forming ability of  $\text{PbBr}_2$  melts which contained various other halides have been investigated. Among the systems studied, the ternary system  $\text{CuCl-CsBr-PbBr}_2$  showed a relatively high glass forming tendency. Brownish-yellow glassy plates 0.5 mm in thickness were obtained by splat cooling between two cold stainless steel plates from some melts in this system. These glasses have glass transition temperatures around  $55^\circ\text{C}$ , crystallization temperatures around  $80^\circ\text{C}$  and show high infra-red transparency over a wide range (up to  $\sim 20\mu\text{m}$ ). The infra-red transmitting properties of these glasses were affected by the glass preparation conditions, especially the melting atmosphere. Fiber fabrication of some glasses in this ternary system was attempted by quenching directly from the low viscosity melt.

15.55            **"Mixed Halide Effect in Fluorozirconate Glasses"**

*Marcel Poulain and J.-L. Adam, U. Rennes, Rennes, France*

Variable amounts of  $\text{NaCl}$  have been included in  $\text{ZrF}_4$  based glasses from the  $\text{ZrF}_4\text{-BaF}_2\text{-ThF}_4$  or  $\text{-LaF}_3$  ternary systems. The evolution of characteristic temperatures ( $T_g$ ,  $T_c$ ,  $T_m$ ), density and refractive index will be given with respect to chlorine concentration. The U.V. absorption edge and the multiphonon absorption edge are shifted toward longer wavelengths with increasing  $\text{Cl}^-$  content. The shift in the I.R. edge is expected from the dilution effect arising from the chlorine incorporation. Assuming that the  $\alpha$  value is proportional to the Zr and F concentration, theoretical values are computed. However, they are still much higher than the experimental value. At 5 microns, extrapolated values correspond to  $\alpha_{th} = 55 \text{ dB/km}$  and  $\alpha_{ex} = 13 \text{ dB/km}$ . This mixed halide effect is discussed in the view of the I.R. absorption spectra between 200 and  $800 \text{ cm}^{-1}$ .

16.15            **Conclusion of Symposium**

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